

# Missing linkers: an alternative pathway to UiO-66 electronic structure engineering

Arthur De Vos,<sup>†</sup> Kevin Hendrickx,<sup>†,‡</sup> Pascal Van Der Voort,<sup>‡</sup> Veronique Van Speybroeck,<sup>\*,†</sup> and Kurt Lejaeghere<sup>\*,†</sup>

<sup>†</sup>*Center for Molecular Modeling (CMM), Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium*

<sup>‡</sup>*Center for Ordered Materials, Organometallics and Catalysis, Department of Inorganic and Physical Chemistry (COMOC), Ghent University, Krijgslaan 281 (S3), 9000 Ghent, Belgium*

E-mail: Veronique.VanSpeybroeck@ugent.be; Kurt.Lejaeghere@ugent.be

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## S1 Ionic model for all node configurations

An ionic model is applied to all node configurations, assuming oxygen atoms to adopt a noble gas configuration and all Zr atoms to be equivalent (see Sec. 2.2 of the main article). Tab. S1 compares the resulting Zr charges in terms of the deviation from the ideal  $+4 e$  charge. It also displays the global charge deviation on every octahedral face of the node. Zr atoms are indicated using the convention proposed in Fig. S1.

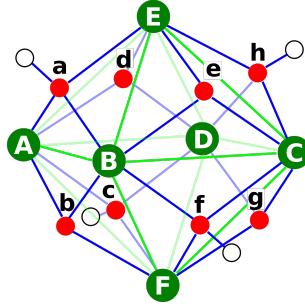


Figure S1: Structure of the node and nomenclature for the Zr atoms used in the ionic model.

Table S1: Charge variations of the Zr atoms relative to the  $+4 e$  ideal value for all node configurations and the global charge variation on every octahedral face. The Zr nomenclature of Fig. S1 is used.

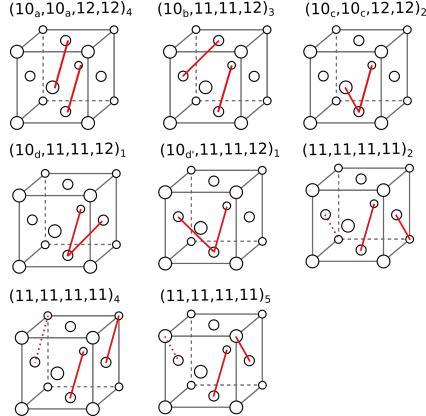
Node	Missing linkers	$\Delta q$ (unit $e$ )													
		A	B	C	D	E	F	ABE	BCE	CDE	ADE	ABF	BCF	CDF	ADF
11	BC	0	-1/6	-1/6	0	0	1/3	-1/6	-1/3	-1/6	0	1/6	0	1/6	1/3
10 <sub>a</sub>	AD, BC	-1/6	1/6	1/6	-1/6	0	0	0	1/3	0	-1/3	0	1/3	0	-1/3
10 <sub>b</sub>	BE, CF	1/3	1/6	-1/6	0	-1/6	-1/6	1/3	-1/6	-1/3	1/6	1/3	-1/6	-1/3	1/6
10 <sub>c</sub>	AB, BC	-1/6	-1/3	-1/6	0	1/3	1/3	-1/6	-1/6	1/6	1/6	-1/6	-1/6	1/6	1/6
10 <sub>d</sub>	BC, BE	1/3	-1/3	-1/6	0	-1/6	1/3	-1/6	-2/3	-1/3	1/6	1/3	-1/6	1/6	2/3
10 <sub>d'</sub>	AB, BE	-1/6	-1/3	1/3	0	-1/6	1/3	-2/3	-1/6	1/6	-1/3	-1/6	1/3	2/3	1/6
9 <sub>a</sub>	AD, BC, CD	-1/6	-1/6	-1/3	-1/3	1/3	2/3	0	-1/6	-1/3	-1/6	1/3	1/6	0	1/6
9 <sub>b</sub>	BE, BF, CD	1/3	-1/3	1/6	-1/6	1/6	-1/6	1/6	0	1/6	1/3	-1/6	-1/3	-1/6	0
9 <sub>c</sub>	AD, BF, CE	-1/6	-1/6	1/6	1/6	-1/6	1/6	-1/2	-1/6	1/6	-1/6	-1/6	1/6	1/2	1/6
9 <sub>d</sub>	BC, BE, BF	1/3	-5/6	1/6	1/3	1/6	-1/6	-1/3	-1/2	2/3	5/6	-2/3	-5/6	1/3	1/2
9 <sub>e</sub>	BC, BF, CE	1/3	-1/3	-1/3	1/3	1/6	-1/6	1/6	-1/2	1/6	5/6	-1/6	-5/6	-1/6	1/2
9 <sub>f</sub>	AE, BF, DE	1/3	1/6	-1/2	1/6	0	-1/6	1/2	-1/3	-1/3	1/2	1/3	-1/2	-1/2	1/3
9 <sub>f'</sub>	AD, BC, BF	-1/3	-1/6	-1/6	2/3	1/6	-1/6	-1/3	-1/6	1/6	2/3	-2/3	-1/2	1/3	1/2
9 <sub>g</sub>	BE, CD, CF	1/3	1/6	-1/3	-1/6	1/6	-1/6	2/3	0	-1/3	1/3	1/3	-1/3	-2/3	0
9 <sub>g'</sub>	AE, BE, CD	-1/6	1/6	1/6	-1/6	-1/3	1/3	-1/3	0	-1/3	-2/3	1/3	2/3	1/3	0
9 <sub>h</sub>	BC, BE, CE	1/3	-1/3	-1/3	1/3	-1/3	1/3	-1/3	-1	-1/3	1/3	1/3	-1/3	1/3	1
9 <sub>h'</sub>	BC, BF, CF	1/3	-1/3	-1/3	1/3	2/3	-2/3	2/3	0	2/3	4/3	-2/3	-4/3	-2/3	0
9 <sub>i</sub>	BE, BF, CE	1/3	-1/3	1/6	1/3	-1/3	-1/6	-1/3	-1/2	1/6	1/3	-1/6	-1/3	1/3	1/2
9 <sub>i'</sub>	AE, BE, BF	-1/6	-1/3	2/3	1/3	-1/3	-1/6	-5/6	0	2/3	-1/6	-2/3	1/6	5/6	0

## S2 Classification of defect structures

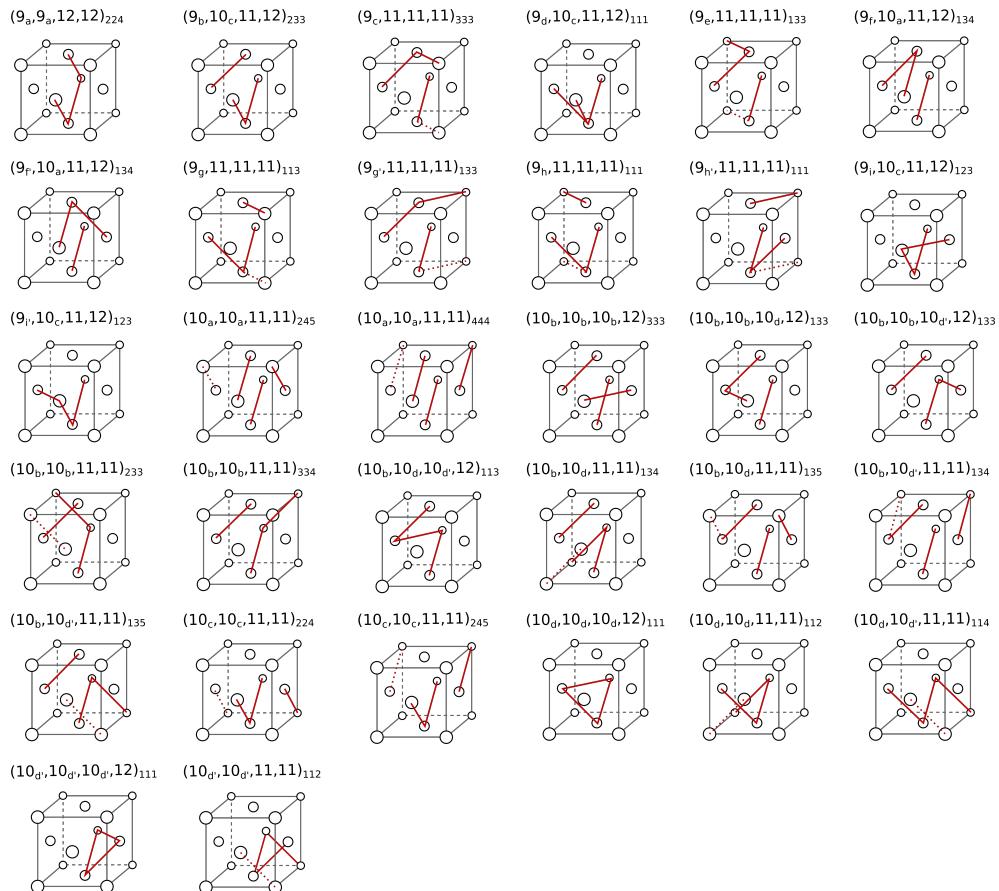
In Table S2 the general defect structure notation introduced in this paper is compared to previous work of Vandichel et al.,<sup>1</sup> Rogge et al.<sup>2</sup> and Bristow et al.<sup>3</sup> Fig. S2 shows a schematic representation of every generated defect structure accompanied by its notation.

Table S2: Comparison of the general notation introduced in this work for the pristine, one-, two- and three-defect structures in a 4-node unit cell to previous classifications.

	Vandichel et al. <sup>1</sup>	Rogge et al. <sup>2</sup>	Bristow et al. <sup>3</sup>	This work
0 missing linkers	A	-	-	(12,12,12,12)
1 missing linker	-	0	-	(11,11,12,12)
2 missing linkers	B	6	8/8	(10 <sub>a</sub> ,10 <sub>a</sub> ,12,12) <sub>4</sub>
	J	4	7/7	(10 <sub>b</sub> ,11,11,12) <sub>3</sub>
	G	2	4/4	(10 <sub>c</sub> ,10 <sub>c</sub> ,12,12) <sub>2</sub>
	LH	1	1/1	(10 <sub>d</sub> ,11,11,12) <sub>1</sub>
	L	1'	2/5	(10 <sub>d'</sub> ,11,11,12) <sub>1</sub>
	H	3	6/6	(11,11,11,11) <sub>2</sub>
	C	5	5/3	(11,11,11,11) <sub>4</sub>
	I	7	3/2	(11,11,11,11) <sub>5</sub>
3 missing linkers	-	-	31/32	(9 <sub>a</sub> ,9 <sub>a</sub> ,12,12) <sub>224</sub>
			18/23	(9 <sub>b</sub> ,10 <sub>c</sub> ,11,12) <sub>233</sub>
			32/29	(9 <sub>c</sub> ,11,11,11) <sub>333</sub>
			11/15	(9 <sub>d</sub> ,10 <sub>c</sub> ,11,12) <sub>111</sub>
			6/7	(9 <sub>e</sub> ,11,11,11) <sub>133</sub>
			13/8	(9 <sub>f</sub> ,10 <sub>a</sub> ,11,12) <sub>134</sub>
			22/22	(9 <sub>f'</sub> ,10 <sub>a</sub> ,11,12) <sub>134</sub>
			4/4	(9 <sub>g</sub> ,11,11,11) <sub>133</sub>
			25/26	(9 <sub>g'</sub> ,11,11,11) <sub>133</sub>
			1/1	(9 <sub>h</sub> ,11,11,11) <sub>111</sub>
			3/6	(9 <sub>h'</sub> ,11,11,11) <sub>111</sub>
			9/10	(9 <sub>i</sub> ,10 <sub>c</sub> ,11,12) <sub>123</sub>
			21/25	(9 <sub>i'</sub> ,10 <sub>c</sub> ,11,12) <sub>123</sub>
			28/16	(10 <sub>a</sub> ,10 <sub>a</sub> ,11,11) <sub>245</sub>
			29/12	(10 <sub>a</sub> ,10 <sub>a</sub> ,11,11) <sub>444</sub>
			26/20	(10 <sub>b</sub> ,10 <sub>b</sub> ,10 <sub>b</sub> ,12) <sub>333</sub>
			12/5	(10 <sub>b</sub> ,10 <sub>b</sub> ,10 <sub>d</sub> ,12) <sub>133</sub>
			27/31	(10 <sub>b</sub> ,10 <sub>b</sub> ,10 <sub>d'</sub> ,12) <sub>133</sub>
			23/24	(10 <sub>b</sub> ,10 <sub>b</sub> ,11,11) <sub>233</sub>
			30/21	(10 <sub>b</sub> ,10 <sub>b</sub> ,11,11) <sub>334</sub>
			8/9	(10 <sub>b</sub> ,10 <sub>d</sub> ,10 <sub>d'</sub> ,12) <sub>113</sub>
			7/2	(10 <sub>b</sub> ,10 <sub>d</sub> ,11,11) <sub>134</sub>
			16/14	(10 <sub>b</sub> ,10 <sub>d</sub> ,11,11) <sub>135</sub>
			14/19	(10 <sub>b</sub> ,10 <sub>d'</sub> ,11,11) <sub>134</sub>
			20/18	(10 <sub>b</sub> ,10 <sub>d'</sub> ,11,11) <sub>135</sub>
			17/17	(10 <sub>c</sub> ,10 <sub>c</sub> ,11,11) <sub>224</sub>
			24/30	(10 <sub>c</sub> ,10 <sub>c</sub> ,11,11) <sub>245</sub>
			19/11	(10 <sub>d</sub> ,10 <sub>d</sub> ,10 <sub>d</sub> ,12) <sub>111</sub>
			5/13	(10 <sub>d</sub> ,10 <sub>d</sub> ,11,11) <sub>112</sub>
			2/3	(10 <sub>d</sub> ,10 <sub>d'</sub> ,11,11) <sub>114</sub>
			10/27	(10 <sub>d'</sub> ,10 <sub>d'</sub> ,10 <sub>d'</sub> ,12) <sub>111</sub>
			15/28	(10 <sub>d'</sub> ,10 <sub>d'</sub> ,11,11) <sub>112</sub>



(a) 2-missing-linker defect structures



(b) 3-missing-linker defect structures

Figure S2: Schematic representation of defect structures with one, two and three missing linkers in a 4-node unit cell.

### S3 Calculation of the node energies

Table S3 displays the design and output matrix used for the least-squares fit to obtain the energy attributed to the different node coordinations. The least-squares fit is performed for all defect structures simultaneously (see Tab. S3 and S4). In this fit all node energies are expressed relative to that of a 12-fold coordinated node, leaving the defect-free node with a zero energy by definition.

Table S3: Number of nodes of a given type in a particular defect structure. The DFT defect energy (rightmost column) is expressed via a least-squares procedure as a sum of energies of the constituent nodes (see Tab. S4).

Defect structure	12	11	$10_a$	$10_b$	$10_c$	$10_d$	$10_{d'}$	$9_a$	$9_b$	$9_c$	$9_d$	$9_e$	$9_f$	$9_{f'}$	$9_g$	$9_{g'}$	$9_h$	$9_{h'}$	$9_i$	$9_{i'}$	$E_{form}$ (eV)	
(11,11,12,12)	2	2																				4.323
(10 <sub>a</sub> ,10 <sub>a</sub> ,12,12) <sub>4</sub>	2		2		1																	9.131
(10 <sub>b</sub> ,11,11,12) <sub>3</sub>	1	2																				8.634
(10 <sub>c</sub> ,10 <sub>c</sub> ,12,12) <sub>2</sub>	2				2		1															8.287
(10 <sub>d</sub> ,11,11,12) <sub>1</sub>	1	2						1														8.728
(10 <sub>d'</sub> ,11,11,12) <sub>1</sub>	1	2							1													8.667
(11,11,11,11) <sub>2</sub>			4																			8.689
(11,11,11,11) <sub>4</sub>			4																			9.168
(11,11,11,11) <sub>5</sub>			4																			8.577
(9 <sub>a</sub> ,9 <sub>a</sub> ,12,12) <sub>224</sub>	2								2			1										12.541
(9 <sub>b</sub> ,10 <sub>c</sub> ,11,12) <sub>233</sub>	1	1						1														12.470
(9 <sub>c</sub> ,11,11,11) <sub>333</sub>			3																			12.837
(9 <sub>d</sub> ,10 <sub>c</sub> ,11,12) <sub>111</sub>	1	1						1														12.738
(9 <sub>e</sub> ,11,11,11) <sub>133</sub>			3																			12.839
(9 <sub>f</sub> ,10 <sub>a</sub> ,11,12) <sub>134</sub>	1	1	1																			13.208
(9 <sub>f'</sub> ,10 <sub>a</sub> ,11,12) <sub>134</sub>	1	1	1																			12.649
(9 <sub>g</sub> ,11,11,11) <sub>113</sub>			3																			12.924
(9 <sub>g'</sub> ,11,11,11) <sub>133</sub>			3																			12.849
(9 <sub>h</sub> ,11,11,11) <sub>111</sub>			3																			12.843
(9 <sub>h'</sub> ,11,11,11) <sub>111</sub>			3																			13.350
(9 <sub>i</sub> ,10 <sub>c</sub> ,11,12) <sub>123</sub>	1	1						1														12.495
(9 <sub>j</sub> ,10 <sub>c</sub> ,11,12) <sub>123</sub>	1	1						1														12.654
(10 <sub>a</sub> ,10 <sub>a</sub> ,11,11) <sub>245</sub>	2	2						1														12.891
(10 <sub>a</sub> ,10 <sub>a</sub> ,11,11) <sub>444</sub>	2	2						3														12.900
(10 <sub>b</sub> ,10 <sub>b</sub> ,10 <sub>b</sub> ,12) <sub>333</sub>	1			2				1														12.998
(10 <sub>b</sub> ,10 <sub>b</sub> ,10 <sub>d</sub> ,12) <sub>133</sub>	1			2					1													13.050
(10 <sub>b</sub> ,10 <sub>b</sub> ,10 <sub>d'</sub> ,12) <sub>133</sub>	1			2					1													12.961
(10 <sub>b</sub> ,10 <sub>b</sub> ,11,11) <sub>233</sub>	2			2						1												13.007
(10 <sub>b</sub> ,10 <sub>b</sub> ,11,11) <sub>334</sub>	2			2						1												12.976
(10 <sub>b</sub> ,10 <sub>a</sub> ,10 <sub>d'</sub> ,12) <sub>113</sub>	1			1				1		1												13.062
(10 <sub>b</sub> ,10 <sub>d</sub> ,11,11) <sub>134</sub>	2			1					1													13.063
(10 <sub>b</sub> ,10 <sub>d</sub> ,11,11) <sub>135</sub>	2			1					1													12.936
(10 <sub>b</sub> ,10 <sub>d'</sub> ,11,11) <sub>134</sub>	2			1						1												12.997
(10 <sub>b</sub> ,10 <sub>d'</sub> ,11,11) <sub>135</sub>	2			1						1												12.912
(10 <sub>b</sub> ,10 <sub>d</sub> ,11,11) <sub>135</sub>	2			1						1												12.651
(10 <sub>c</sub> ,10 <sub>c</sub> ,11,11) <sub>224</sub>	2				2					2												12.554
(10 <sub>c</sub> ,10 <sub>c</sub> ,11,11) <sub>245</sub>	2				2					3												13.247
(10 <sub>d</sub> ,10 <sub>d</sub> ,10 <sub>d</sub> ,12) <sub>111</sub>	1				2					2												13.167
(10 <sub>d</sub> ,10 <sub>d</sub> ,11,11) <sub>112</sub>	2				1					1												13.046
(10 <sub>d</sub> ',10 <sub>d</sub> ',10 <sub>d</sub> ',12) <sub>114</sub>	2				1					3												13.071
(10 <sub>d</sub> ',10 <sub>d</sub> ',10 <sub>d</sub> ',12) <sub>111</sub>	1				2					2												13.035
(10 <sub>d</sub> ',10 <sub>d</sub> ',11,11) <sub>112</sub>	2																					

Table S4: Node energies calculated from a least-squares fit to all defect structures containing one, two and three missing linkers in a 4-node unit cell (see Tab. S3).

Node	Energy (eV)	Energy/linker (eV)
12	0	0
11	2.174	2.174
$10_a$	4.371	2.185
$10_b$	4.313	2.157
$10_c$	4.133	2.066
$10_d$	4.403	2.202
$10_{d'}$	4.344	2.172
$9_a$	6.271	2.090
$9_b$	6.163	2.054
$9_c$	6.315	2.105
$9_d$	6.431	2.144
$9_e$	6.317	2.106
$9_f$	6.663	2.221
$9_{f'}$	6.104	2.035
$9_g$	6.402	2.134
$9_{g'}$	6.327	2.109
$9_h$	6.321	2.107
$9_{h'}$	6.828	2.276
$9_i$	6.188	2.063
$9_{i'}$	6.347	2.116

## S4 Density of states

### S4.1 Defect-free, 1-, 2- and 3-defect structures

In Fig. S3 and Fig. S4 all calculated densities of states are shown for the defect structures bearing one, two and three missing linkers in a 4-node unit cell.

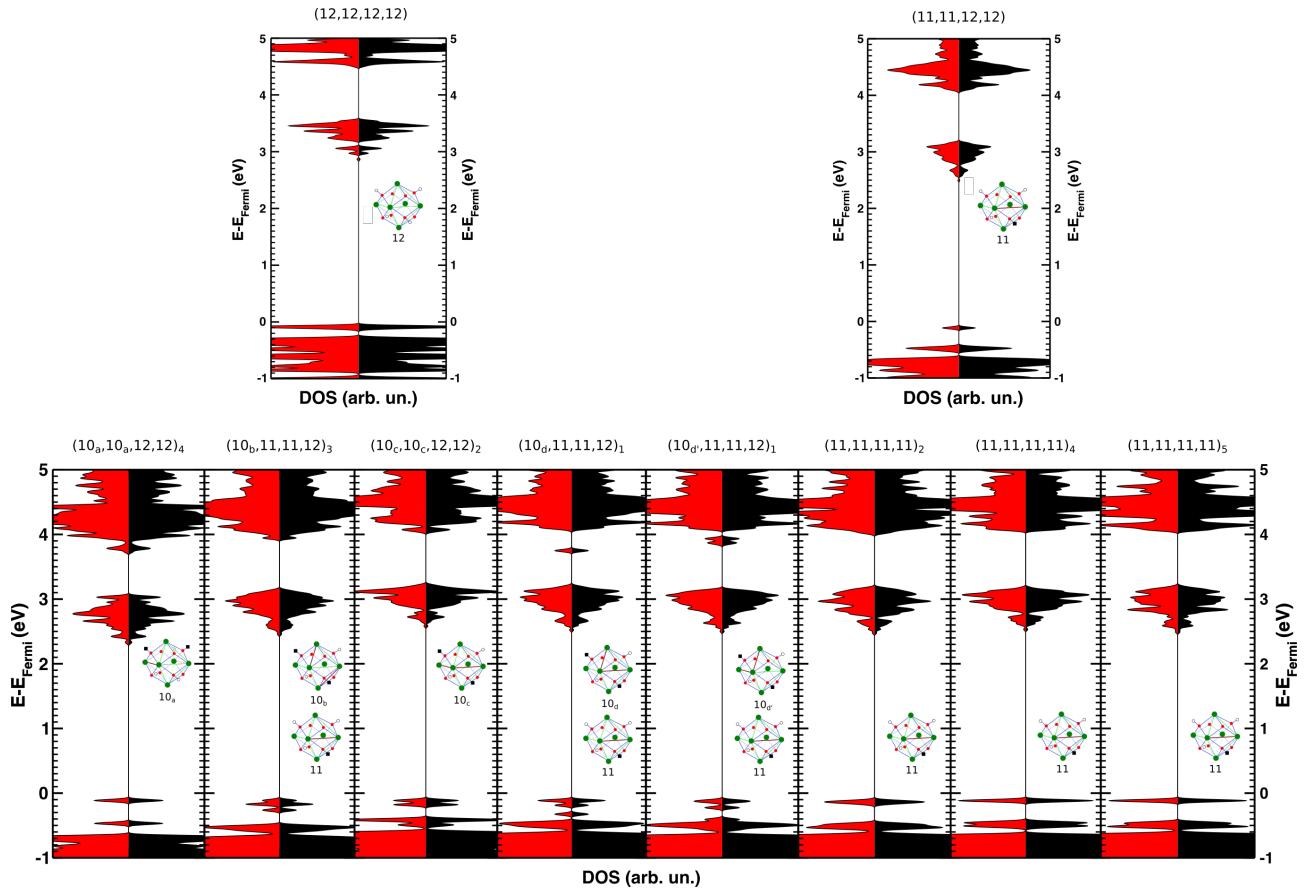


Figure S3: Densities of states for defect structures with 0, 1, 2 missing linkers in a 4-node unit cell. Red and black curves represent different spin channels and all DOS are aligned with respect to the fermi energy.

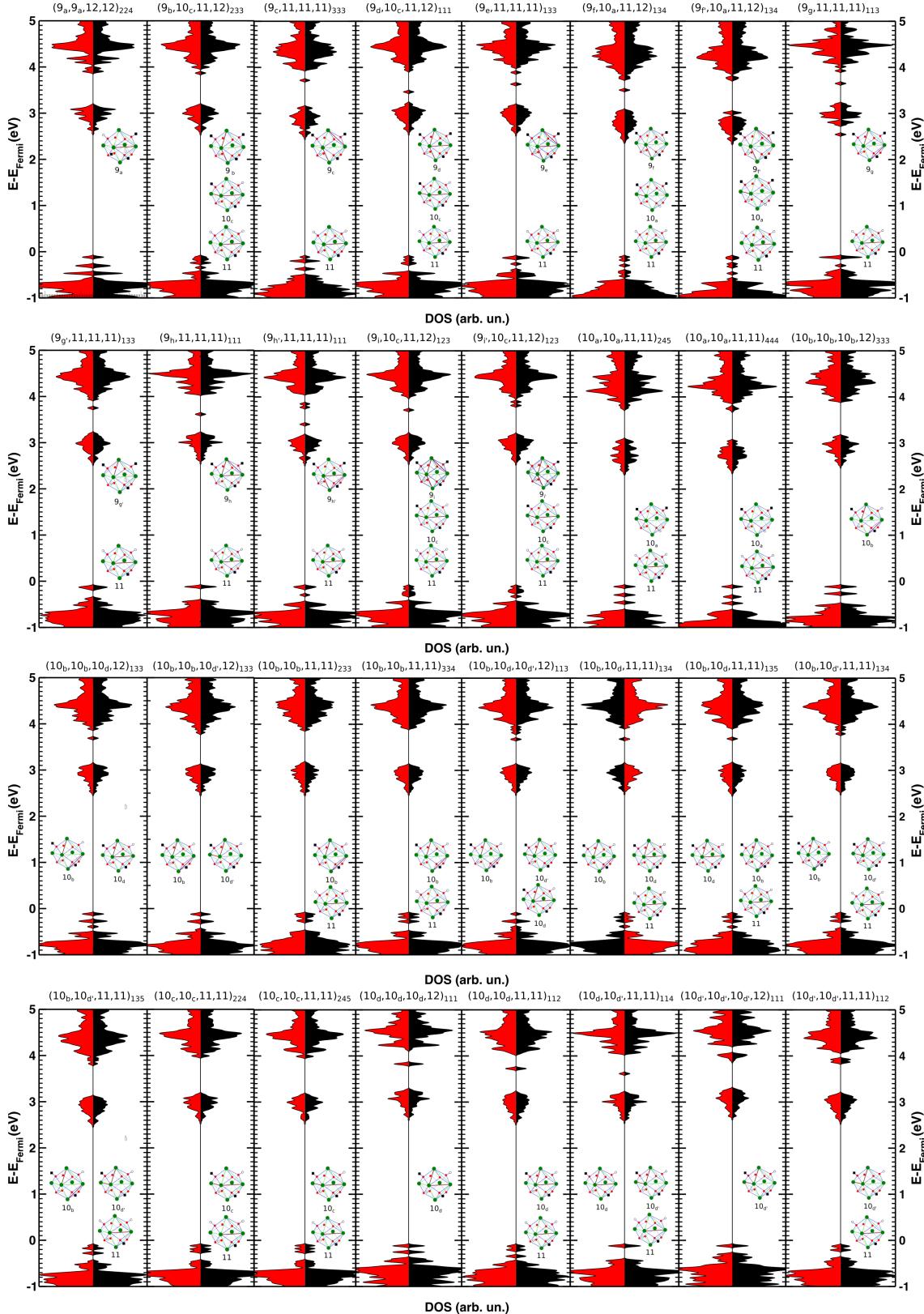


Figure S4: Densities of states for defect structures with 3 missing linkers in a 4-node unit cell. Red and black curves represent different spin channels and all DOS are aligned with respect to the fermi energy.

## S4.2 Missing node compared to 4-defect structure

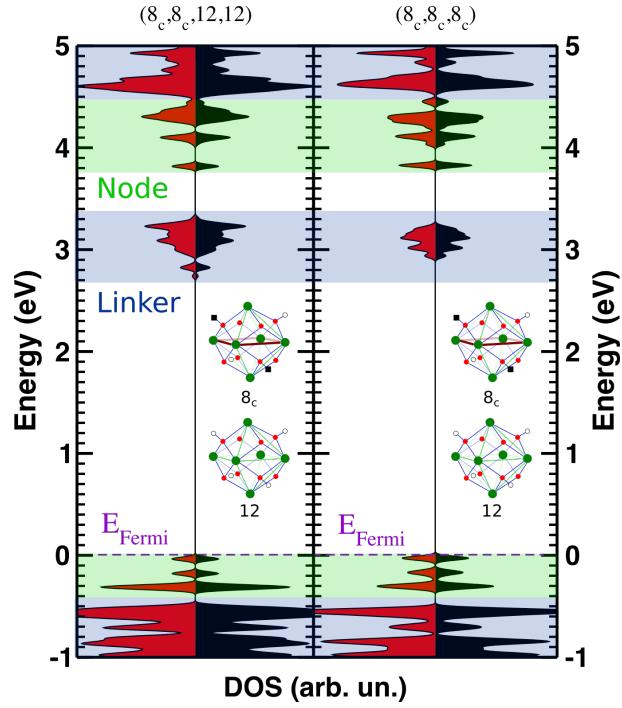


Figure S5: Removal of a node from the 4-node unit cell (right) compared to a 4-defect structure in which the linkers are removed to created corresponding node configurations present in a missing node defect structure (left). Red and black curves represent different spin channels and all DOS are aligned with respect to the pristine  $\mu\text{-OH}_2\text{O}$  node states. Blue and green indicate linker and node states, respectively.

### S4.3 Isovivalent substitution

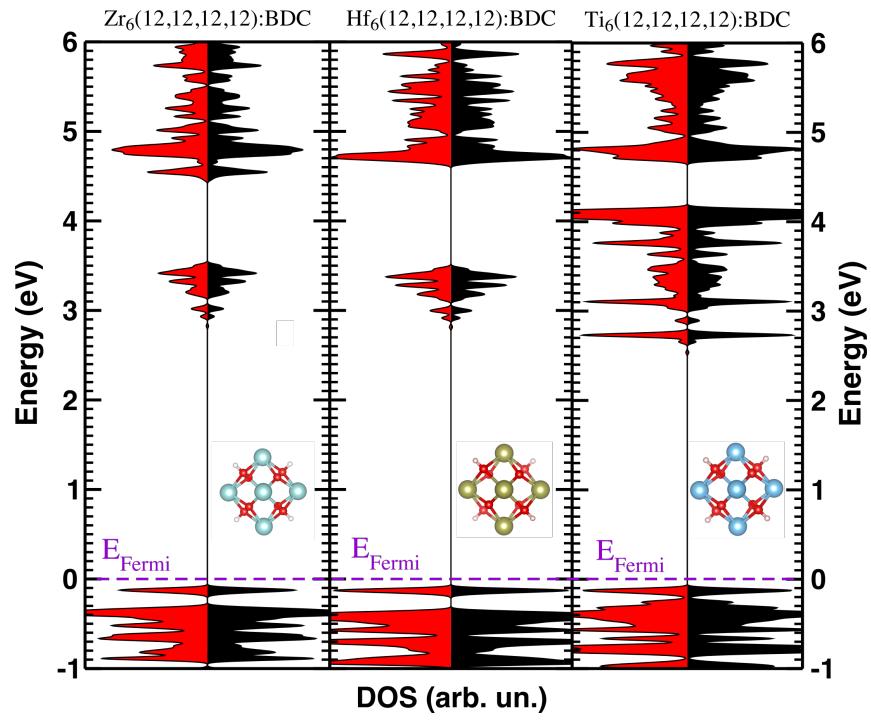


Figure S6: Densities of states of UiO-66(Zr), UiO-66(Hf) and UiO-66(Ti). Red and black curves represent different spin channels and all DOS are aligned with respect to the pristine  $\mu\text{-OH}_2\text{O}$  node states.

#### S4.4 Amino and nitro functionalization

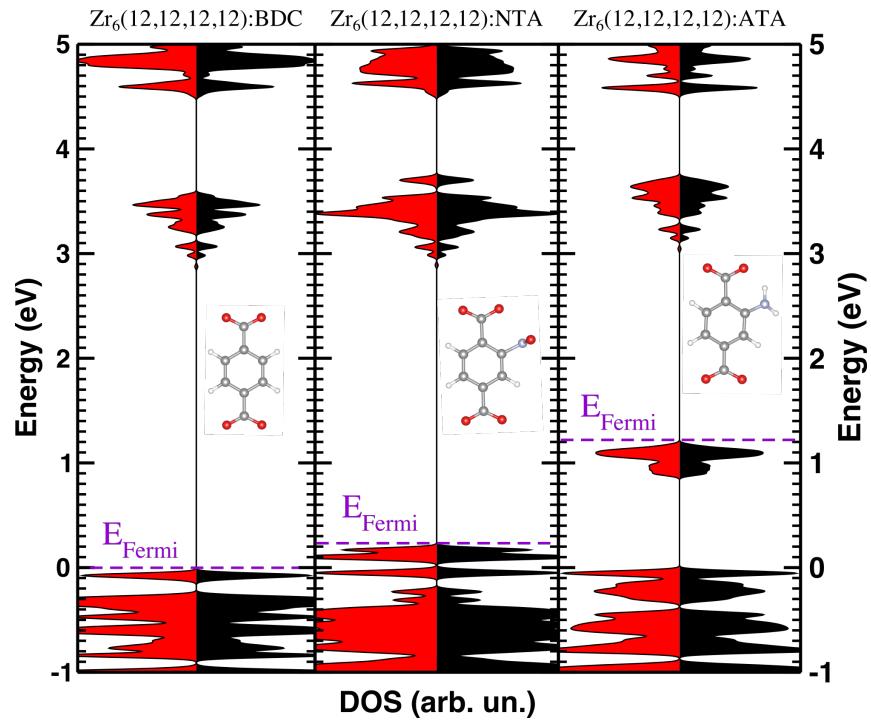


Figure S7: Densities of states for UiO-66 type materials where no linkers have been modified and where the linkers have been functionalized with one nitro (NTA, nitrotetraphthalate) or amino (ATA, aminotetraphthalate) group per linker. Red and black curves represent different spin channels and all DOS are aligned with respect to the pristine  $\mu\text{-OH}_2\text{O}$  node states.

#### S4.5 Linker length

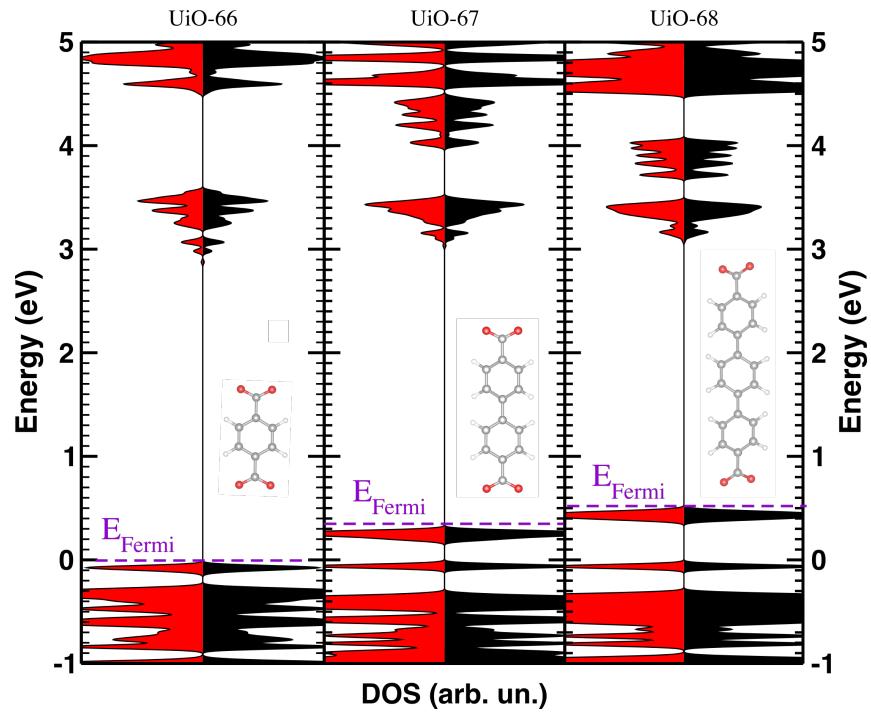


Figure S8: Densities of states of UiO-66(Zr), UiO-67(Zr) and UiO-68(Zr). Red and black curves represent different spin channels. Red and black curves represent different spin channels and all DOS are aligned with respect to the pristine  $\mu\text{-OH}_2\text{O}$  node states.

#### S4.6 Orthogonal electronic structure engineering

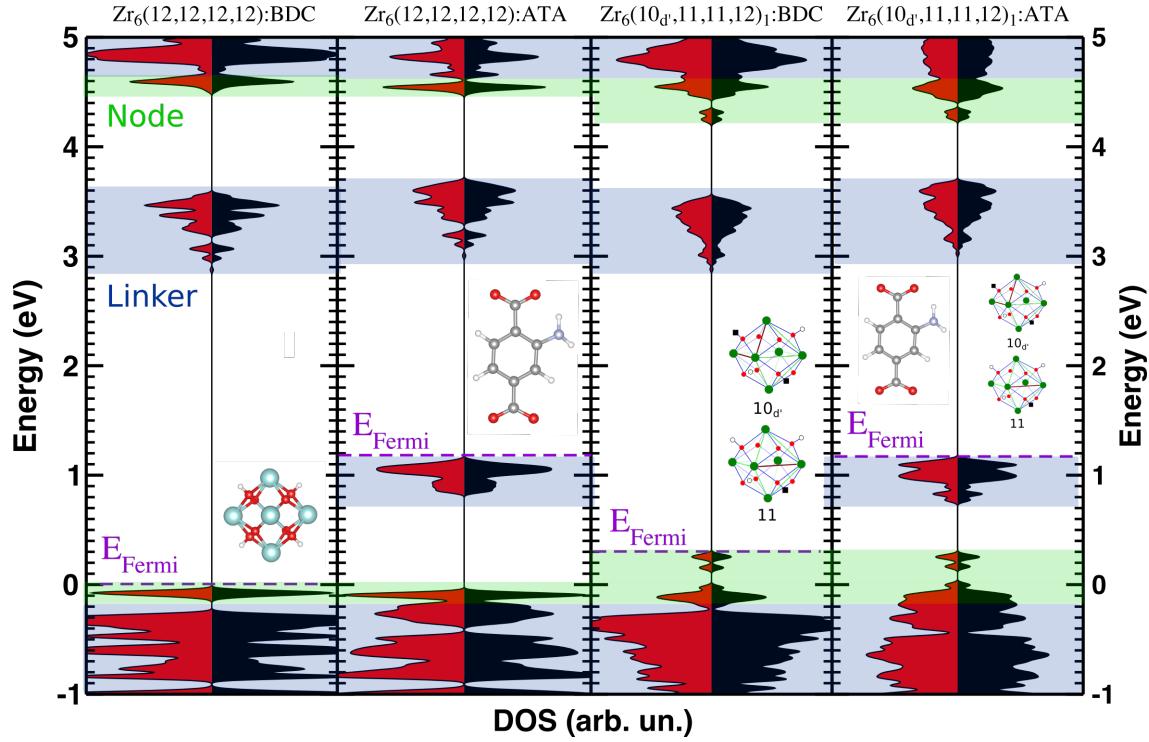


Figure S9: Linker and node modifications showing the idea of orthogonal electronic structure engineering. Red and black curves represent different spin channels and all DOS are aligned with respect to the pristine  $\mu\text{-OH}_2$  node states. Blue and green indicate linker and node states, respectively.

#### S5 $\Delta E_{abs}$ and $\Delta E_{LMCT}$

Table S5: Values for  $\Delta E_{LMCT}$  and  $\Delta E_{abs}$  (eV, see Fig. 1 of the main manuscript) for isovalently substituted UiO-66 with Zr, Ti and Hf, functionalized UiO-66(Zr) with nitro and amino functionalized groups and UiO-66,67,68(Zr) with changing linker length.

Structure	$\Delta E_{abs}$ (eV)	$\Delta E_{LMCT}$ (eV)
UiO-66(Zr)	3.08	1.73
UiO-66(Hf)	3.08	2.23
UiO-66(Ti)	3.25	-0.36
UiO-67(Zr)	2.68	1.73
UiO-68(Zr)	2.56	1.73
UiO-66(Zr)-NO <sub>2</sub>	2.65	1.78
UiO-66(Zr)-NH <sub>2</sub>	1.81	1.63

## S6 Orbital localization

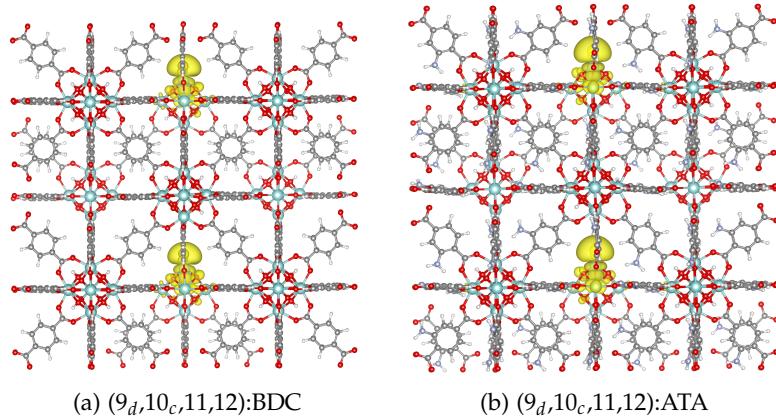


Figure S10: Lowest unoccupied d-orbital in the  $(9_d, 10_c, 11, 12)$ :BDC and  $(9_d, 10_c, 11, 12)$ :ATA structure (see Fig. 10 of the main manuscript).

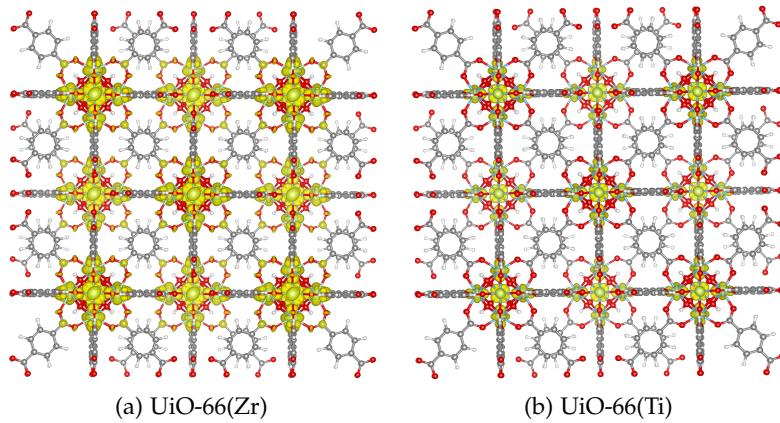


Figure S11: Lowest unoccupied d-orbital in the UiO-66(Zr) and UiO-66(Ti) showing a similar character whereas for UiO-66(Ti) its spatially less extended due to its 3d instead of 4d orbitals.

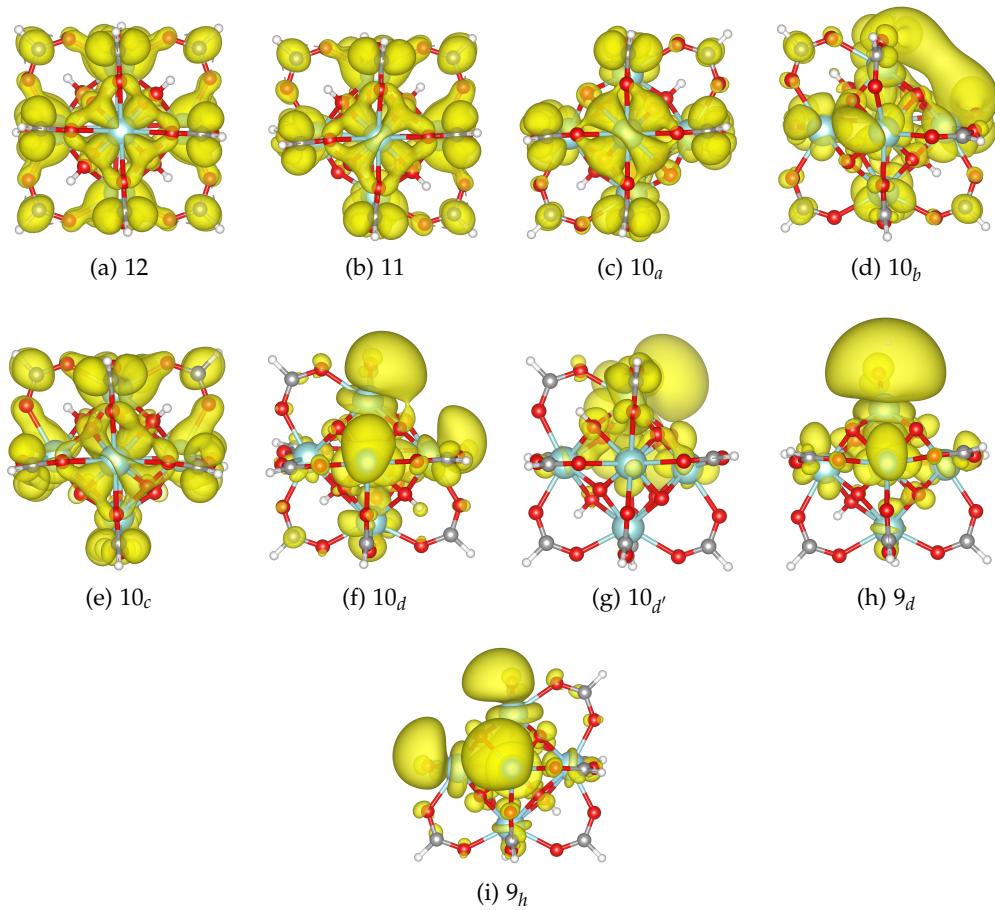


Figure S12: The SOMO of calculated cluster configurations with one surplus electron.

## References

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